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Examination of Mechanisms and Fuel-Molecular  
Effects on Soot Formation

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Examination of Mechanisms and Fuel-Molecular  
Effects on Soot Formation

Annual Report

I. SUMMARY

A variety of hydrocarbons has been pyrolyzed in a single-pulse shock tube over the temperature range of 1000 to 2400K and for dwell times of approximately 700 microseconds. Gas samples of reactant, intermediate, and final products were collected and analyzed using gas chromatography. Experimental data were used in conjunction with a computer model to develop (or confirm existing) detailed chemical kinetic models for several of the hydrocarbons that were pyrolyzed. Model results agreed well with experimental data not only for the decomposition of the parent compound and formation of low molecular weight products, but also for the formation of single-ring aromatic species. These latter processes are believed to lead to the formation of polycyclic aromatic hydrocarbons, soot precursors, and eventually soot.

II. INTRODUCTION

The production of soot in diffusion flames, such as that existing in gas turbine engines, is directly related to the chemical nature of the fuel. In addition, research has shown recently that chemical kinetic processes control the growth of polynuclear aromatics and probably the formation of soot precursors. The production rate of soot precursors, in turn, limits the production rate of the number of soot particles and hence effects the total mass of soot produced. This work focuses on obtaining experimental data on the pyrolysis and oxidative pyrolysis of hydrocarbons under soot-forming conditions. A single-pulse shock tube has been selected for the experimental tool since it is one of the few devices capable of obtaining detailed information on product distribution over the range of 1200 to 2400K in an environment free from complications due to diffusional effects. Using the experimental data and single-pulse information obtained from other work, detailed chemical kinetic mechanisms describing the pyrolysis of a variety of hydrocarbons are being developed. Chemical mechanisms describing the formation of aromatic hydrocarbons (from aliphatic hydrocarbons) are included in the model.



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### III. STATEMENT OF WORK

United Technologies Research Center shall furnish the level of effort, including all related services, facilities, supplies and materials, needed to:

- a. Select a variety of hydrocarbon fuels for pyrolysis and oxidative pyrolysis. The selection will be subject to approval by the AFOSR technical manager and will be based in part on preliminary results from the experimental and modeling phases of this program.
- b. Pyrolyze and/or oxidatively pyrolyze a variety of hydrocarbons and/or mixtures of hydrocarbons in the single-pulse shock tube. Test conditions will vary from approximately 1200 to 2500K, dwell times of 500 to 800 microseconds, and total pressures of 4 to 8 atmospheres. Approximately 18-22 mixtures will be shock-heated and examined. For each mixture, approximately twenty individual shocks will be run.
- c. Examine data and quantitatively determine concentrations of parent hydrocarbons, intermediates and final products; collate the data from each series of runs and prepare data for analysis; estimate soot and/or PAH formation based on mass balance of observable species.
- d. Evaluate experimental data to determine chemical mechanisms and kinetic rates.
- e. Identify species and mechanisms leading to the formation of soot (or soot precursors).
- f. Develop detailed chemical kinetic mechanisms and operate a shock tube version of the CHEMKIN code.
- g. Construct a detailed model describing soot formation and growth in a diffusion-free environment.
- h. Make comparisons between experimental data and model predictions.
- i. Incorporate recent advances in the chemical kinetics of hydrocarbon pyrolysis and pre-particle mechanisms of soot formation into computer models.

## IV. STATUS OF WORK

## (A) Experimental Effort

During this past year, eleven separate series of single-pulse shock tube experiments have been completed. Each series represents a collection of individual shock tube experiments along with chemical analysis of reactant and products for a given initial reactant condition (species, initial concentration). The eleven series are listed in Table I along with six similar experiments which have been conducted under a corporate sponsored program at UTRC. For each series, shock strengths were varied to produce a range in initial post-shock temperature from approximately 1100 to 2400K. Examples of profiles of the parent hydrocarbon as well as product species are shown in the Appendices to this annual report.

Collection of new experimental pyrolysis results was stopped for the period August to November 1985 in order to upgrade the existing gas chromatographic system. This upgrade was performed under corporate-sponsorship and now enables full analysis of not only the  $C_1$  to  $C_{10}$ -hydrocarbons, hydrogen and oxygen, but also the analysis of the carbon oxides ( $CO$  and  $CO_2$ ) at parts-per-million concentration levels using catalytic hydrogenation. In addition, the ability to quantitatively analyze methane and the  $C_2$ -hydrocarbons has been enhanced by a duplication in measurements; that is, these species are separated and measured on capillary and packed columns. The proper operation of the upgraded analytical system is presently being verified by a series of experiments using acetaldehyde as a reactant since the decomposition kinetics of acetaldehyde have been established previously. Preliminary results demonstrate the system is performing better than expected with run-to-run and even day-to-day repeatability better than 1%.

## IV. (B) MODEL EFFORT

## (1) Code Enhancement

Much of the enhancement to the computer codes used in this contract have been made under a corporate-sponsored program. Yet the advancements significantly enhance the rate of progress in the present contract work and therefore will be described briefly.

Chemical kinetic modeling is performed using CHEMKIN, LSODE, and a shock tube code for CHEMKIN originally written by personnel at Sandia National Laboratories. As described in the proposal for this contract, the original shock tube code had already been modified in-house in order to model the quenching process in a single-pulse shock tube. During the past year, the code has been modified or a new code developed to:



- (1) automatically plot species profiles as a function of time (for a given initial temperature) or as a function of temperature (for a given dwell time);
- (2) automatically calculate and plot dominant contributions from every reaction to the net formation or net destruction of each species, as a function of reaction time; and
- (3) calculate absolute values and expressions for reverse rate constants and equilibrium constants for a given forward rate constant and given set of thermodynamic data.

These enhancements to the computer code may not generally appear as highlights in a publication or a presentation, but are of great value to meeting the overall research objectives of this program.

#### IV. (B) MODEL EFFORT

##### (2) Chemical Kinetic Modeling

Detailed chemical kinetic modeling has been performed for acetylene, vinylacetylene, and benzene during this past year. Details of this work are described in Appendices I-IV and need not be repeated here. One important result of this work is that aromatics can be produced during the pyrolysis of acetylene through a sequence of addition reactions. Based on previous work at other laboratories, these types of reactions are key to the formation of soot precursors. The good comparisons of experimental and modeling results in the present work represents the first experimental confirmation of such models in a pyrolytic system at elevated temperatures. The overall model is shown in Table II. Strong support is seen for this mechanism from the pyrolysis of acetylene (which produces  $C_4H_4$  and  $C_6H_6$  as intermediate products). Parallel processes are observed during the pyrolysis of vinylacetylene. Also of importance is that the route proposed for benzene pyrolysis in Appendix IV follows the path of the curved arrow and is consistent with both experimental data and thermodynamics. Previous proposals had fallen short of simultaneously satisfying these constraints.

TABLE I  
Series of Experiments Completed  
During First Year of Program

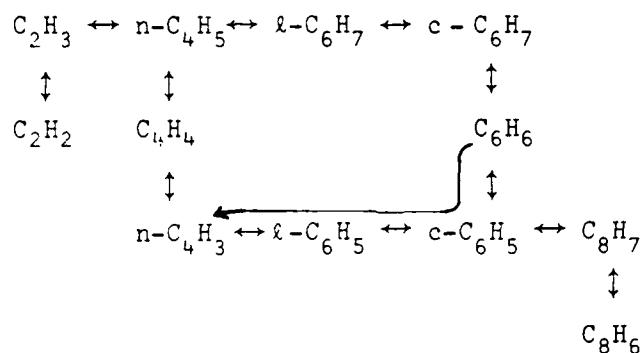
<u>Reactant</u>	<u>Initial Concentration</u>
Benzene, $C_6H_6$	0.12%
" "	0.012%
Vinylacetylene, $C_4H_4$	1.0%
" "	0.11%
" "	0.01%
$C_2H_2/C_6H_6$	0.82%/0.06%
" "	0.115%/0.0085%
" "	0.016%/0.0012%
Acetylene	4.9%
"	0.6%
"	0.069%
Toluene, $C_7H_8$	* 0.05%
" "	* 0.035%
" "	* 0.016%
" "	* 0.0175%
$C_2H_2/C_7H_8$	* 3.3%/0.51%
Acetaldehyde, $CH_3CHO$	* 0.105%

\*Research conducted under corporate-sponsored program.

All fuels were diluted in argon and (except for the experiments on pure toluene) were conducted at total pressures of approximately six to nine atmospheres.

TABLE II

Model for Production of First Aromatic Ring from Acetylene



Vertical translation represents addition or loss of an H-atom and horizontal translation represents addition or loss of acetylene (except for the conversion between linear and cyclic compounds).

## V. LIST OF PUBLICATIONS

A paper entitled "Single-Pulse Shock Tube Examination of Hydrocarbon Pyrolysis and Soot Formation" by M. B. Colket, III, was presented to the Fifteenth International Symposium on Shock Waves and Shock Tubes at the University of California, Berkeley, California, on July 29 to August 1, 1985. A manuscript of the paper is included in Appendix I and will be published in a volume of the proceedings of this meeting.

An article entitled "Pyrolysis of Acetylene, Vinylacetylene and Benzene in a Single-Pulse Shock Tube" will be written for submission to the Twenty-First Symposium (International) on Combustion for presentation at its meeting in Munich, August 1986, and for publication in proceedings of the meeting. The paper will be authored by M. B. Colket, III, and should be completed by January 15, 1986.

An article entitled "Pyrolysis of Toluene in a Single-Pulse Shock Tube" has been started by M. B. Colket and D. J. Seery and should be completed in the spring of 1986 for submission to Combustion and Flame.

## VI. MEETING INTERACTIONS

In addition to the paper presented at the Shock Tube Symposium (see List of Publications), several papers have been or will be presented at meetings. They include:

- \*1. "Addition of Methyl and Vinyl Radicals to Benzene," by M. B. Colket, III, Eastern Section of the Combustion Institute, Clearwater Beach, Florida, December 1984. (Appendix II)
- \*2. "Pyrolysis of Acetylene in a Single-Pulse Shock Tube," by M. B. Colket, III. International Conference on Chemical Kinetics, National Bureau of Standards, Gaithersburg, MD, June 1985. (Poster Session)
- 3. "Pyrolysis of Vinylacetylene," by M. B. Colket, III, Eastern Section of the Combustion Institute, Philadelphia, PA, Nov. 4-6, 1985. (Appendix III)
- 4. "Pyrolysis of Benzene," by M. B. Colket, III, Division of Fuel Chemistry, New York City National Meeting, American Chemical Society, April 13-16, 1986. (Appendix IV)

\*Corporate sponsored research.

Copies of extended abstracts which appear in preprints of the meeting are included as appendices to this report.

Of potential interest is a concrete example of the value of interaction at meetings. A (not-fully satisfactory) mechanism for the observed production of vinylacetylene during acetylene pyrolysis was presented (item #2) at the International Conference on Chemical Kinetics. Discussions with a variety of people, particularly Dr. S. Stein of NBS, led the author to retract this proposal, and support the mechanism as listed in Table II, which is both kinetically and thermodynamically much more reasonable.

#### VII. NEAR-TERM PLANS

Planned for the present (1986) contract year are pyrolysis experiments on ethylene and styrene, mixtures of hydrocarbons. Of particular interest is addition of methyl radicals (source:  $(\text{CH}_3\text{CO})_2$ ) to the pyrolysis of other hydrocarbons, e.g. acetylene or benzene.<sup>3</sup> Addition of methyl radicals is expected to provide interesting results since several combustion systems have demonstrated that methane addition strongly accelerates soot formation. Oxidation studies using the new analytical capabilities are also planned.

Modeling efforts will include studies of the pyrolytic reactions associated with the hydrocarbons studied in the single-pulse shock tube. In addition, growth reactions from single-ring to polycyclic aromatic hydrocarbons will be examined.

Computer codes will be enhanced so that initiation and termination processes can be readily identified and so that the effects of these processes can be easily examined. Secondly, the codes will be modified to identify reactions which are (nearly) equilibrated and those which dominate in the forward or reverse direction.

SINGLE-PULSE SHOCK TUBE EXAMINATION OF HYDROCARBON  
PYROLYSIS AND SOOT FORMATION

by

M. B. Colket, III  
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A single-pulse shock tube coupled to a capillary gas chromatograph has been used to observe the pyrolysis of a variety of hydrocarbons. Product species, mass balances, and H/C ratios of uncollected material have been determined. Relative "sooting" tendencies have been found to be toluene > benzene > allene > vinylacetylene > acetylene > 1,3-butadiene > cyclohexene for similar carbon-atom densities. A detailed chemical kinetic model has been constructed for the pyrolysis of acetylene and describes profiles of major species as well as the production of vinylacetylene, benzene and phenylacetylene.

## Introduction

Shock tubes are frequently used for studying kinetics and mechanisms of both hydrocarbon pyrolysis and soot formation at conditions characteristic of diffusion flames. Single-pulse shock tubes (SPST) have been used perhaps most successfully for measuring rates of primary decomposition processes when fractional decomposition of the parent hydrocarbon is small<sup>1</sup>. Its applications to the study of soot may be limited by wall quenching and finite quenching in the rarefaction wave; but the potential for providing detailed species information with the aid of capillary gas chromatography has motivated the present research.

The ultimate goal of the experimental work is to provide data from which mechanisms of hydrocarbon pyrolysis and soot formation can be obtained. As part of that goal the relative tendency of different hydrocarbons to soot in a SPST is measured in this work. In addition, an objective of this paper is to extend a recent proposal<sup>2</sup> and present some results related to soot formation during the pyrolysis of acetylene. Specifically, experimental and modeling results on the production of vinylacetylene (VA), benzene, and phenylacetylene (PA) are shown.

## Description of Facilities

The SPST used in this program is 258 cm long and has a diameter of 3.8 cm (i.d.). The driver is 88 cm in length and can be tuned by shortening its length in 3.8 cm increments; the driven section is 197 cm long. Pre-stressed aluminum diaphragms were used to control the rupture pressure. An 11.7 liter "dump tank" is located in the driver (lower pressure) section 30 cm downstream of the diaphragm. The pumping station is located at this tee. Pressure profiles were determined using Kistler pressure transducers located 15.25 and 2.50 cm from the end wall. Arrival times were determined to within one microsecond using

digitized pressure traces. Calculated quench rates are typically  $10^5$  K/sec in the rarefaction wave. Starting pressures prior to filling are  $0.2\mu$  and leak rates are less than  $1\mu/\text{min}$ . Post-shock temperatures were calculated based on the measured incident shock velocity and normal shock wave equations.

The procedures for performing an experiment are similar to those described by Tsang<sup>1</sup>, except for an automated sampling system. The sample is collected at the endwall of the shock tube using 0.045 inch i.d. tubing heated to over 85 C. Approximately 30 milliseconds after the gas has been shock heated and cooled, a solenoid valve opens to the evacuated sample cell and then closes after 300 milliseconds. All valves and lines in this system have been degreased and rinsed in toluene to minimize condensation on the walls. The sample storage vessel is all stainless steel with an internal volume of 25 cc. Total internal volume of the remainder of the sampling system is less than 3 cc.

The sampling volume is directly coupled to a low volume, heated inlet system of a Hewlett Packard 5880 A gas chromatograph. Typical injection pressures are 0.5 atmospheres and are measured to within two percent using a calibrated pressure transducer. One gas sampling valve injects samples onto a 25 m x 0.33 mm i.d. CP Sil 5 CB (1 micron film thickness) fused silica capillary column (from Chrompack Inc.) followed by quantitative hydrocarbon analysis using a flame ionization detector. A second valve leads to a silica gel packed, stainless-steel column and a single-filament, modulated thermal conductivity detector for analysis of hydrogen. Valves, detectors and software integration routines enable this system to provide automatic quantitative detection of hydrogen and hydrocarbon species up to  $C_{10}$ -hydrocarbons. Based on repeated injections of calibrated samples, overall measurement accuracies are estimated to be approximately three percent. Calibration gases were stored in stainless steel cylinders with degreased valves and were heated to approximately 60C prior to injection.

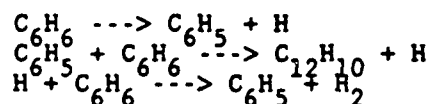
Argon (99.999% pure) was obtained from Matheson and was the principal diluent. Other chemicals were at least 99.5% pure according to gas chromatographic analysis, except for vinylacetylene, allene, and acetylene. VA contained approximately 8000 ppm of an unidentified  $C_5$ -hydrocarbon. Allene was obtained from several different vendors yet was typically 87 to 93% pure with a variety of other  $C_3$ -hydrocarbons as impurities. Bulb-to-bulb distillation enhanced the purity level to approximately 97%. Similarly, the initial concentration of acetone in acetylene was reduced from approximately 2% of the initial acetylene to about 1000 ppm.

## Results

Toluene, benzene, cyclohexene, 1,3-butadiene, VA, allene, and acetylene have been pyrolyzed in a bath of argon. For each hydrocarbon, a series of shock tube runs were performed. Densities<sup>18</sup> behind the reflected shock wave range were approximately  $1.8 \times 10^{-8}$  carbon atoms/cc. Reflected shock temperatures and pressures ranged from approximately 1100 to 2500 K and 5 to 8 atmospheres, respectively. Dwell times were typically 550 to 800 microseconds although for the bulk

of runs, dwell times were close to 700 microseconds. Typical results are shown in Figs. 1a and 1b for the pyrolysis of 1.17% benzene in argon. Presented in these figures are the final product distribution (for 18 separate shocks) after the test gas has been shock heated and then quenched by the rarefaction wave. The general features, i.e., production of aromatics over the 1500 to 1900 K temperature range, and the dominance of hydrogen and 'equilibrium' concentrations of the acetylenes above 2200 K is apparent in virtually all fuels. For the non-aromatic fuels, equilibrium concentrations are generally achieved above 1900 to 2000 K. At temperatures below 1500 to 1600 K, the product distribution is controlled by the kinetics of the decomposition of the hydrocarbon parent.

Figure 1 exhibits a relatively large amount of hydrogen produced at low temperatures. Modeling demonstrates that this 'low temperature' hydrogen is principally formed via the sequence:



A comparable amount of biphenyl should be produced, yet is unobserved due to its apparent loss during the sampling process or in the inlet system to the gas chromatograph. The amount of carbon converted to biphenyl at 1400 K would be approximately a few percent of the total and is consistent with the measured mass balance. Total hydrogen and carbon mass balances have been determined for the data in Fig. 1 and are plotted in Fig. 2. Also shown are calculated H/C ratios of the missing material. (Uncertainties in this calculation are obviously large when either hydrogen or carbon are nearly fully recovered.) At low temperatures, the ratio is in reasonable agreement with the assumption that biphenyl (H/C = 0.825) or other small multi-ringed compounds are produced. At higher temperatures, the H/C ratio is very low, suggesting the formation of very large polynuclear aromatics (PAH) or even soot. The low ratio of 0.1 observed in these benzene experiments is atypical since for most other hydrocarbons, the H/C ratio of the missing material ranges from 0.2 to 0.3 above 1700 K. This difference between benzene and other hydrocarbons may not be significant in light of the potential errors in calculating the H/C ratios of the missing material.

The fractional mass recovered is a strong function of both the concentration and the density of the parent hydrocarbon. The effect of hydrocarbon type on mass balance is shown in Fig. 3. Assuming that the mass loss is indicative of soot productions, the relative tendency to soot is approximately toluene  $\gtrsim$  benzene  $>$  allene  $>$  VA  $\gtrsim$  acetylene  $>$  1,3-butadiene  $\gtrsim$  cyclohexene. The single-pulse shock tube data is in excellent agreement with the relative tendencies to soot and with the temperature dependence as determined using optical absorption. The detailed species profiles offer some insight to the relative sooting tendencies. Production of aromatics, particularly PA, appears to be critical. Allene, for example, produces large quantities of benzene and PA. The conversion of allene to benzene is as high as 25% of the initial carbon (and 4% to PA). If some benzene is converted to PAH and possibly soot, then the actual production of benzene may be even larger.



Thus the "sooting" tendency of allene is quite similar to those of the aromatics. In comparison, only 9% of the initial butadiene carbon is converted to benzene and the production of PA is delayed (relative to its production during benzene or allene pyrolysis) by 100 to 150 K. The similarity in mass balance between acetylene and VA at elevated temperatures can be explained by the dominant overall chain process  $C_4H_4 + H \rightarrow 2C_2H_2 + H$  apparent from the product distribution during VA pyrolysis. Also of interest are significant concentrations of PA, which are presumably formed via  $C_4H_3$  addition to VA, followed by cyclization and H-atom loss. The production of PA near 1400-1700 K may lead to the significant mass deficit observed in this regime. The similarity between cyclohexene and butadiene is explained by the rapid unimolecular decay  $c-C_6H_{10} \rightarrow 1,3-C_4H_6 + C_2H_4$  and the relatively low sooting tendency for  $C_2H_4$  (ref. 3).

Detailed chemical kinetic modeling has been performed using Chemkin and a modified shock tube code originally developed at Sandia National Laboratories. The modified code includes the capability of modeling the quenching effect of the rarefaction wave in an SPST. The basic kinetic mechanism is similar to modifications<sup>2,4</sup> of a proposed mechanism<sup>5</sup> and as shown in Fig. 4 describes well the distribution of mono-, di-, and triacetylene. The production of VA, benzene and PA is indicated below:

	Log A	E( cal/mole)
$H + C_2H_2 \rightarrow C_2H_3$	12.74	2500.
$C_2H_3 + C_2H_2 \rightarrow NC_4H_5$	13.00	8000.
$NC_4H_5 \rightarrow C_2H_4 + H$	13.70	41400.
$NC_4H_5 + C_2H_2 \rightarrow C_6H_6 + H$	12.60	9000.
$NC_4H_5 + C_2H_2 \rightarrow C_6H_5$	12.48	5000.
$C_6H_5 + C_2H_2 \rightarrow C_8H_6 + H$	12.32	5600.

A in units of cc, moles, sec.

The selection of this reaction sequence and rate constants has been based on a combination of the SPST experimental results and pioneering work at other laboratories<sup>2,6-8</sup>. The experimental and modeling results compare well at low temperature, but suggest some revision may be required at temperatures above 1800 K.

#### Acknowledgments

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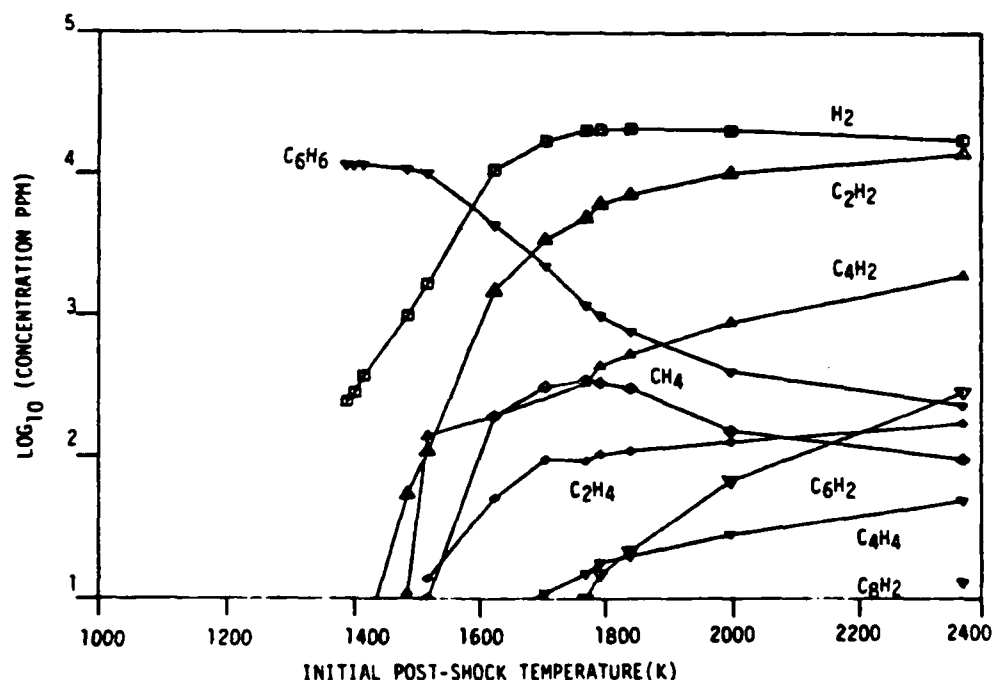


Fig. 1a SPST Pyrolysis of 1.17% Benzene at 6 atmospheres and for 700 microseconds: distribution of aliphatic products.

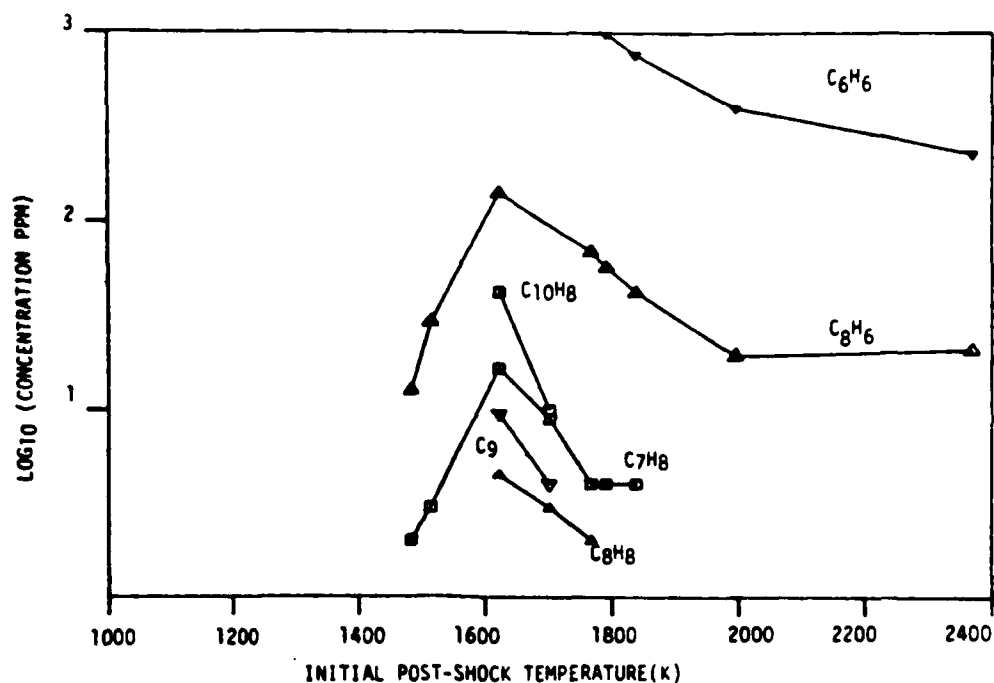


Fig. 1b SPST Pyrolysis of 1.17% Benzene at 6 atmospheres and for 700 microseconds: distribution of aromatic products.

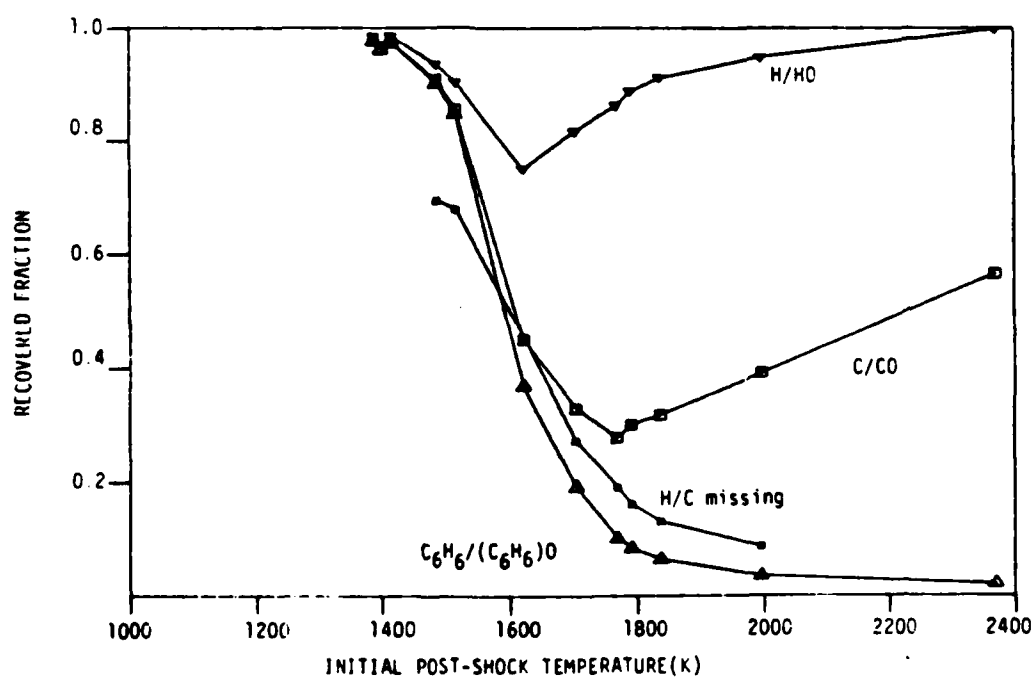


Fig. 2 Fractional recovery of initial hydrogen, carbon, and benzene during pyrolysis of 1.17% Benzene. Also shown is the calculated hydrogen-to-carbon ratio of the uncollected mass.

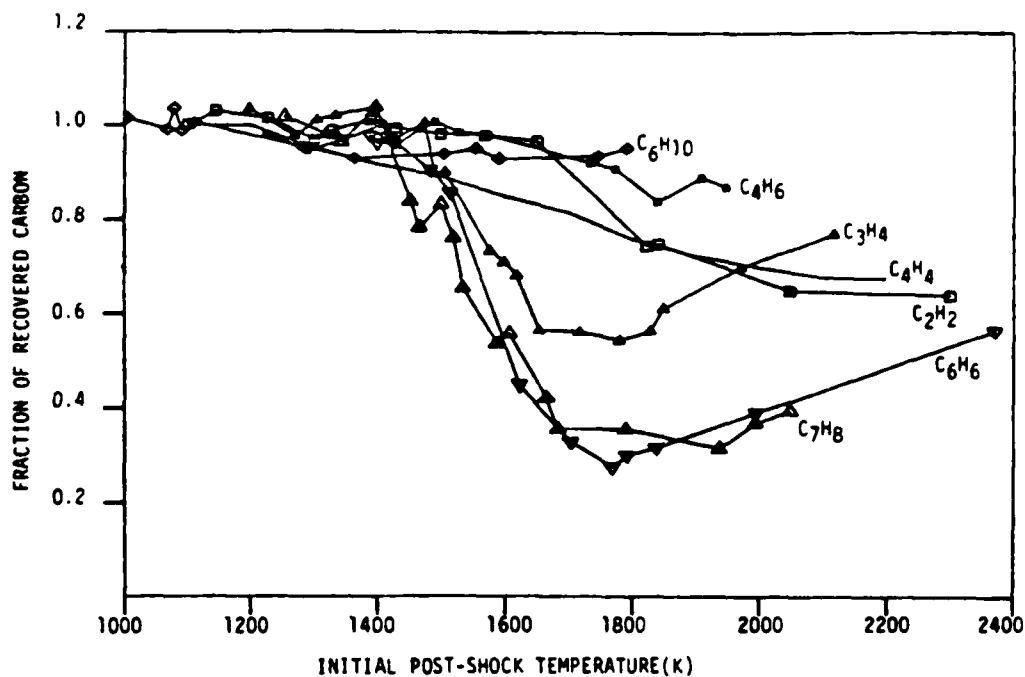


Fig. 3 Fractional carbon recovery for a variety of hydrocarbons at a total pressure and carbon density of approximately 6 atmospheres and  $1.8 \times 10^{18}$  carbon atoms/cc.  $\Delta$ -1.0%  $C_7H_8$ ,  $\nabla$ -1.2%  $C_6H_6$ ,  $\blacktriangle$ -2.3% allene, —-1.75%  $C_4H_4$ ,  $\square$ -3.7%  $C_2H_2$ ,  $\blacksquare$ -1.75% 1,3- $C_4H_6$ ,  $\blacklozenge$ -1%  $C_6H_{10}$ . ( $C_4H_4$  curve is an estimate based on runs at dissimilar concentrations.)

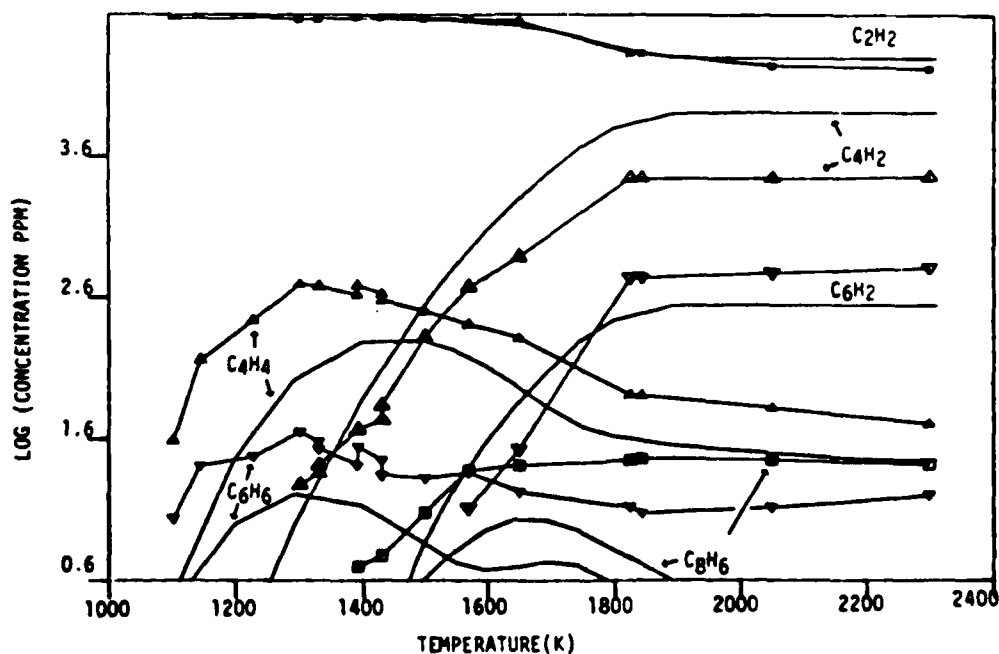


Fig. 4 Experimental and model results for the pyrolysis of 3.7% acetylene.

## ADDITION OF ALKYL HYDROCARBONS TO AROMATIC RINGS

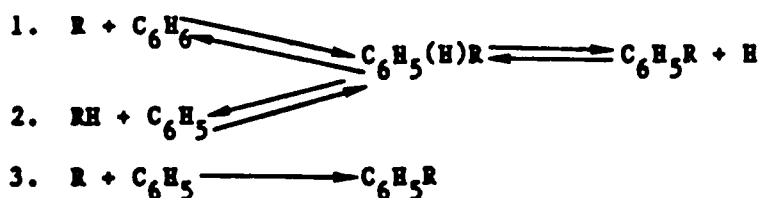
by

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Presentation to ES/CI, December 3-5, 1984  
Clearwater Beach, Florida

The addition of alkyl hydrocarbons to aromatic rings is believed to be important in the growth to polyaromatic hydrocarbons in diffusion flames. To examine this problem, we have pyrolyzed 1,3-butadiene in the presence of benzene using a single-pulse shock tube. Butadiene was selected, since the vinyl radical is an important intermediate during its pyrolysis and since 1,3-butadiene is known to pyrolyze at temperatures significantly below those at which benzene pyrolyzes.

Four series of experiments were performed over the temperature range of approximately 1100 to 2000 K, for dwell times of approximately 700 microseconds, and total pressures of approximately five to seven atmospheres. The concentrations in this series of experiments were (1) 0.175% butadiene; (2) 0.175% butadiene, 1.05% benzene; (3) 0.175% butadiene, 4.6% benzene; and (4) 1.1% benzene with the balance argon. The results of the first of these experiments have been described previously (Colket, 1983). In comparison to the pure butadiene pyrolysis, the presence of benzene does little to perturb the overall pyrolysis reactions below about 1450 K except that significant concentrations of toluene, styrene, and phenylacetylene are formed. Above 1450 K, benzene begins to decompose, a significant deficit from the initial mass is observed, and direct comparisons to the pure pyrolysis is questionable. The production of each of the alkylated aromatics in mixtures (2) and (3) can be compared with their production during the pure pyrolyses of butadiene or benzene in Figures 1-3. These figures clearly show significantly enhanced formation of alkylated aromatics due to the presence of benzene. Types of reactions which may be responsible include:



When R represents  $CH_3$ ,  $C_2H_3$ , or  $C_2H$ , the respective product species are toluene, styrene, and phenylacetylene. It is probable that reactions (1) and (3) can be neglected in the case when  $R = C_2H$  since the ratio  $C_2H/C_2H_2$  can be shown to be very low near 1400 K. Alternatively, some of the phenylacetylene may be produced from the decomposition of styrene.

A surprising experimental result is that an increase in the initial benzene concentration by a factor of about four does not result in a proportional increase in the concentrations of the alkylated aromatics. Very little increase is observed in the case of the toluene or phenylacetylene profiles (below 1450 K) and styrene production is increased only by a factor of 1.5 to 2. The most logical explanation for this result is that the presence of benzene must bring about a significant decrease in concentrations of the alkyl radicals. Furthermore, type 2 reactions are probably not dominant since RH (i.e.,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_4$ ) concentrations are not significantly affected by the presence (or concentration) of benzene, yet an increase in initial benzene concentrations probably results in a corresponding (proportional) increase in phenyl concentrations.

A significant decrease in alkyl radical concentrations can occur if Reactions 1, 3 or  $\text{R} + \text{C}_6\text{H}_6 \longrightarrow \text{RH} + \text{C}_6\text{H}_5$  (4) are fast. Since concentrations of alkylated aromatics are about an order of magnitude less than those of  $\text{C}_1$ - and  $\text{C}_2$ - hydrocarbons, Reactions 1 and 3 can be neglected relative to Reaction 4. Ignoring thermal decomposition and recombination of radicals, Reaction 4 thus should be compared to  $\text{R} + \text{C}_4\text{H}_6 \longrightarrow \text{RH} + \text{C}_4\text{H}_5$  (5).

Reaction 4 should effectively compete with Reaction 5 since the  $\text{C}_6\text{H}_6/\text{C}_4\text{H}_6$  ratios for mixture numbers (2) and (3) are about 6 and 25, and since Reaction 4 is only about 2 kcal/mole greater than Reaction 5 (for the preferred route (Cole, 1982) of extraction of a primary hydrogen).

Assuming that Reaction 4 is the dominant loss mechanism for methyl and vinyl radicals, Reaction 1 is the dominant formation route for toluene and styrene, and that phenylacetylene is formed principally from styrene decomposition, then ratios for  $k_1/k_4$  can be estimated to be the ratio of final concentrations of products, i.e.,  $[\text{C}_6\text{H}_5\text{R}]_f/[\text{RH}]_f$ . For both methyl and vinyl,  $k_1/k_4$  was found to be approximately  $0.3 \pm 0.15$ .

In addition some detailed chemical kinetic modeling has been performed using the shock tube version of the chemkin code (Mitchell and Kee, 1980) but modified to account for the quenching processes in a single-pulse shock tube. The chemical kinetic mechanism proposed by Kiefer, et al, 1984 for butadiene kinetics was used except that the thermal decomposition kinetics of benzene as determined by Fujii and Asaba (1973) were employed. It was found that the profiles for styrene in Figs. 1-3 could be approximately fit regardless of which reaction mechanism was used. The determined rate constants for the vinyl radical when Reactions 1, 2, and 3 were each used individually are  $k_1 < 3.5 \times 10^{10}$ ,  $k_2 < 1.2 \times 10^{11}$ , and  $k_3 < 1.8 \times 10^{13}$  cc/mole-sec and should be considered to be upper limits. These values, however, are critically dependent on the reaction kinetics of the phenyl and vinyl radicals. Additional modeling efforts are in progress to identify which, if any, of the above steps dominate.

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5. Mitchell, R. E. and R. T. Kee: A General-Purpose Computer Code for Predicting Chemical Kinetic Behavior Behind Incident and Reflected Shocks. Sandia National Laboratories, SAND82-8205, March, 1982.

FIG. 1

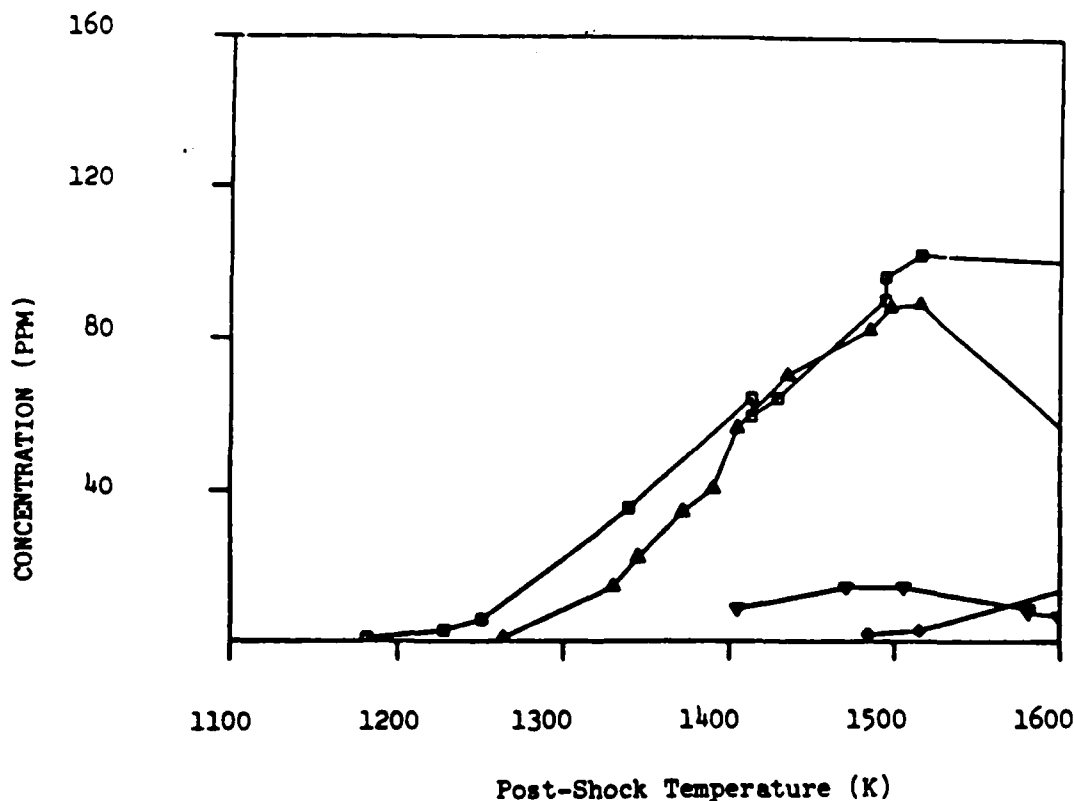


Fig. 1 PRODUCTION OF TOLUENE

□ 0.17% C<sub>4</sub>H<sub>6</sub>, 4.6% C<sub>6</sub>H<sub>6</sub>; Δ 0.175% C<sub>4</sub>H<sub>6</sub>, 1.0% C<sub>6</sub>H<sub>6</sub>  
 ◇ 0.17% C<sub>4</sub>H<sub>6</sub>; ▽ 1.1% C<sub>6</sub>H<sub>6</sub>. Dwell times are approximately 700 microseconds.

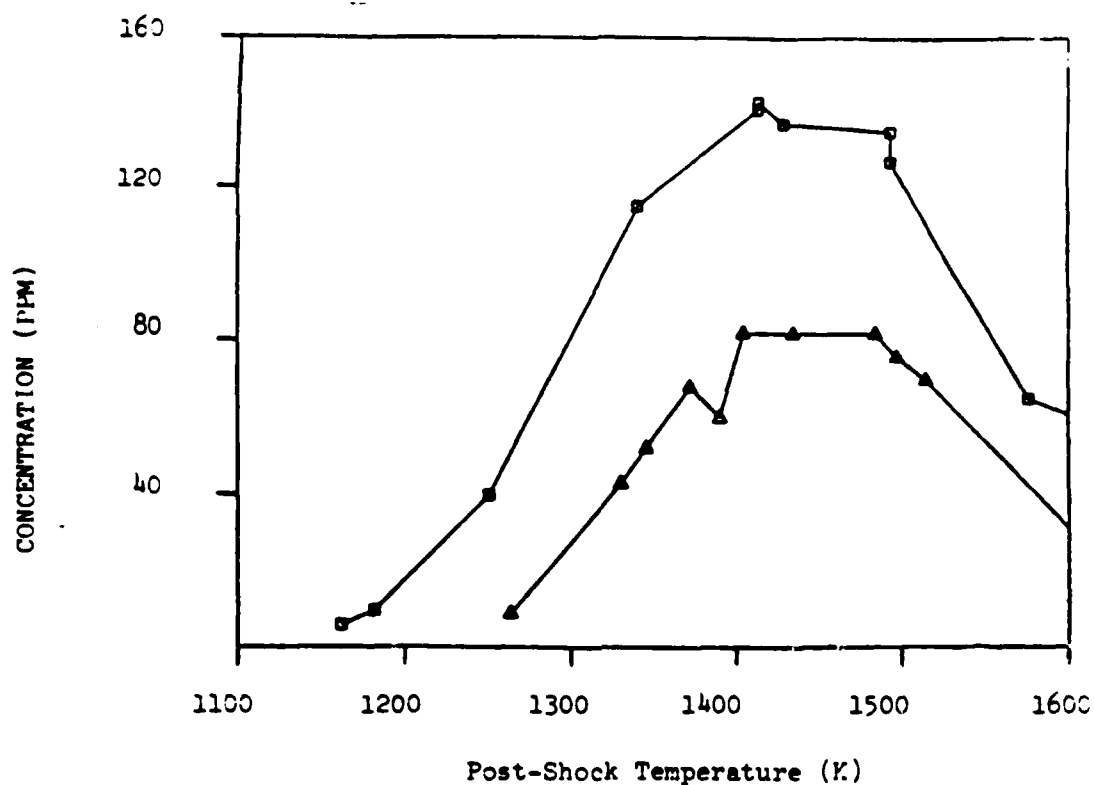


FIG. 2

Fig. 2 PRODUCTION OF STYRENE. See Fig. 1 for symbol identification. Negligible styrene was observed at these temperatures during the pyrolysis of the neat fuels.

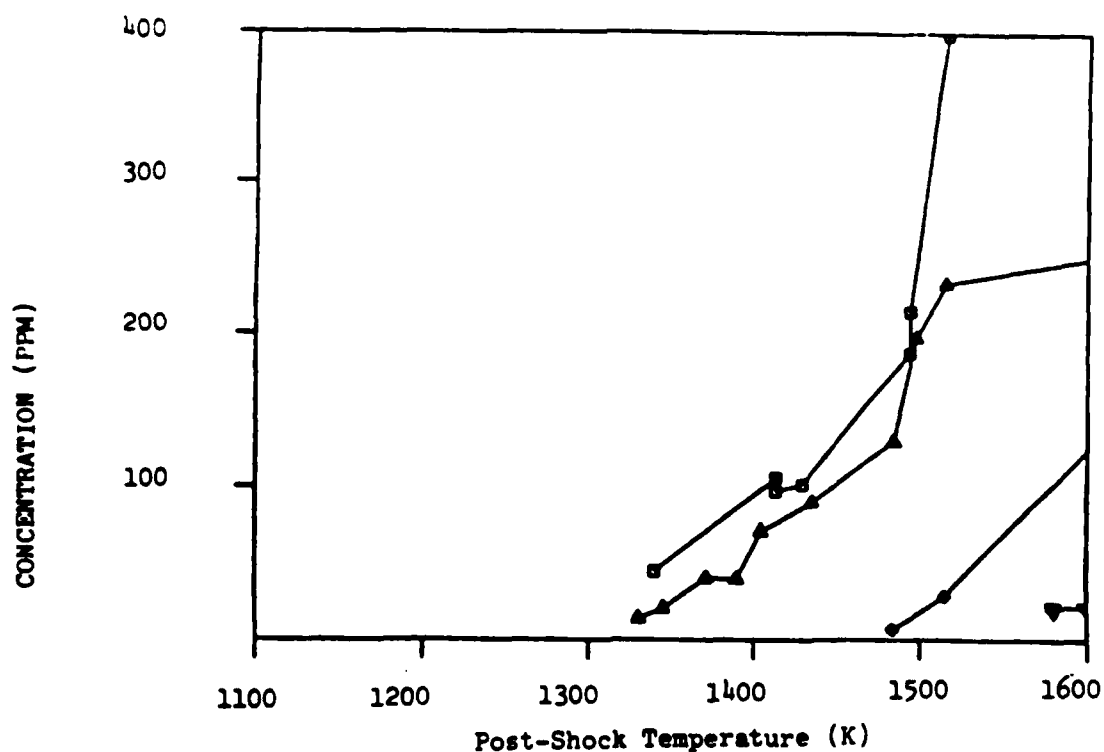


FIG. 3

Fig. 3 PRODUCTION OF PHENYLACETYLENE. See Fig. 1 for symbol identification.



# APPENDIX III

## PYROLYSIS OF VINYLACETYLENE

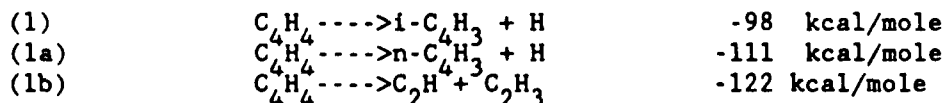
by

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Eastern Section of the Combustion Institute  
Philadelphia, Pa, November 4-6, 1985

Mixtures of 0.01, 0.115, and 1.0% vinylacetylene in argon have been pyrolyzed in a single-pulse shock tube (SPST). Reaction conditions varied from approximately 1100 to 2500 K and 6 to 8 atmospheres and dwell times were about 700 microseconds. Gas samples were collected and analyzed using capillary gas chromatography. Logarithms of the final (quenched) concentrations of stable products are plotted versus initial post-shock temperature in Figs. 1-4. Principal decomposition products at low temperatures and low initial concentrations are acetylene, diacetylene and hydrogen, although acetylene is by far the dominant product. (Hydrogen profiles, although not shown in the figures, are similar to or slightly higher than the profiles for  $C_4H_2$ .) With increasing temperature tri- and tetra-acetylenes are produced. At higher concentrations other products are observed including benzene, styrene, phenylacetylene and species not shown in the figures, e.g. methane, ethylene, methylacetylene, a variety of  $C_5$  compounds,  $C_6H_4$ , toluene, an unidentified  $C_9$  compound, and naphthalene. The carbon balance was  $\pm 5\%$  for the series of 100 and 1150 ppm experiments, although the 1150 ppm series did not extend to elevated temperatures where the largest mass deficits were observed. The mass deficit for the 1% series of experiments was 20-25% at temperatures above 2000 K. The "bell-shape" which has been observed for aromatics was not apparent. Instead, the mass deficit is relatively linear over the temperature range 1400-2000 K and is similar in magnitude and shape to that observed during acetylene pyrolysis at similar concentrations (Ref. 1).

A detailed chemical kinetic model was constructed and model calculations were obtained using a shock tube code (Ref. 2) which has been modified at UTRC to include the effects of the quenching wave in the SPST. The chemical kinetic model principally consists of a model for acetylene pyrolysis which has been based on previous work and has been used to describe recent SPST results (briefly described in Ref. 1). Several reactions specific to the vinylacetylene system were added to this acetylenic mechanism. There are three possible initiation processes:



where the estimated endothermicities may each be in error by as much as 10 to 15 kcal/mole due to uncertainties in heats of formation of the hydrocarbon radicals. In this work, it was assumed that the principal initiation process was Reaction 1 with a rate expression of  $10^{15.2} \exp(-42800/T) \text{ sec}^{-1}$  although the A-factor seems high for the C-H bond scission. It is important to note that the model results were relatively insensitive to the absolute magnitude of the initiation rate or its temperature dependence. A change of a factor of three in the initiation rate resulted in approximately a 20-30%

change in the overall rate of decomposition and the formation of products. The explanation for this phenomena is that the decomposition of vinylacetylene in the range 1200-1400 K is controlled by a Rice-Herzfeld mechanisms:

		$\log_{10} A$	E
(1) initiation	$C_4H_4 \rightarrow i-C_4H_3 + H$	15.2	85000.
(2) chain	$H + C_4H_4 \rightarrow n-C_4H_3 + H_2$	13.13	1379.
(3) chain	$n-C_4H_3 \rightarrow C_2H_3 + C_2H_2$	14.82	45060.
(4) chain	$C_2H_3 \rightarrow H + C_2H_2$	13.0	46000.
(5)	chain termination		

where Reactions 2-4 account for the majority of the decomposition of the parent and the predominance of acetylene in the low-temperature products. (The Arrhenius factors are given in units of cc, moles, sec and cal/mole.) Termination is rapidly equilibrated with initiation and the overall rate is dependent at most on the square root of the initiation rate. Formation of diacetylene is explained by the chain:

(6)	$H + C_4H_4 \rightarrow i-C_4H_3 + H_2$	14.5	14500.
(7)	$i-C_4H_3 \rightarrow C_4H_2 + H$	13.0	52500.

although some  $C_4H_2$  is produced via initiation (Reaction 1) followed by Reaction 7.

Production of benzene and styrene near 1400 K is described by Reactions 2 and 3 followed by:

		$\log_{10} A$	E
(8)	$C_4H_4 + C_2H_3 \rightarrow C_6H_7$ $C_6H_7 \rightarrow c-C_6H_6 + H$ $c-C_6H_6 \rightarrow C_6H_5 + H$	11.30	0.

and

(9)	$C_4H_4 + n-C_4H_3 \rightarrow C_8H_9$ $C_8H_9 \rightarrow c-C_8H_8 + H$ $c-C_8H_8 \rightarrow C_8H_7 + H$	13.6	3000.
-----	--	------	-------

Phenylacetylene is formed principally by

(10)	$C_8H_8 + H \rightarrow C_8H_7 + H_2$ $C_8H_7 \rightarrow C_8H_6 + H$	14.48	7000.
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at low temperatures, although with increasing temperature acetylene addition to phenyl radicals competes. Reactions 8-10 were assumed to be overall processes and non-reversible to simplify the calculations. The value of  $k_9$  appears to be 1 to 2 orders of magnitude higher than expected for a complex process involving addition and cyclization. This rate, however, as well as many others in this system of reactions is highly dependent on the selected thermodynamics and competitive rate processes both of which critically affect the quasi-steady state concentrations of the radicals. In regards to thermodynamics, heats of formation at 300 K used in the present modeling effort for certain species are reproduced in Table 1 and are literature

values. Of note is that the heats of formation of diacetylene and vinyl-like radicals are in general disagreement with values estimated using group additivity techniques. Of specific interest is the necessity of using a high value for the  $\Delta H_f$  of diacetylene in order to predict properly equilibrium values of diacetylene. A value near 108 kcal/mole, which is consistent with group-additivity techniques, results in a significant over prediction of the equilibrium diacetylene concentrations.

The comparison of the experimental data and the model (including chemistry, thermodynamics and quenching processes) is shown in Figs. 1-4 and exhibits an excellent comparison for a wide range of species in spite of a variation of two orders of magnitude in the initial concentration of vinylacetylene.

TABLE I  
Selected Thermodynamics at 300 K

Species	Heat of Formation (kcal/mole)	Entropy (cal/mole/k)
$C_2H$	127.0	49.6
$C_2H_3$	63.4	54.5
$C_2H_2$	111.7	59.9
$i-C_4H_3$	115.2	71.6
$n-C_4H_3$	128.1	67.7
$C_4H_4$	69.4	66.1
$n-C_4H_5$	82.5	69.1
$C_6H_5$	78.5	69.4
$C_6H_6$	19.9	65.2
$C_8H_6$	78.3	79.6
$C_8H_8$	35.2	82.4

#### Acknowledgments

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#### References

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- Mitchell, R.E. and Kee, R.J., "A General-Purpose Computer Code for Predicting Chemical Kinetic Behavior Behind Incident and Reflected Shocks" SAND82-8205, Sandia National Laboratories, March, 1982.

FIGURE 1 100 PPM VINYLACETYLENE PYROLYSIS  
data vs. model, 700 microseconds

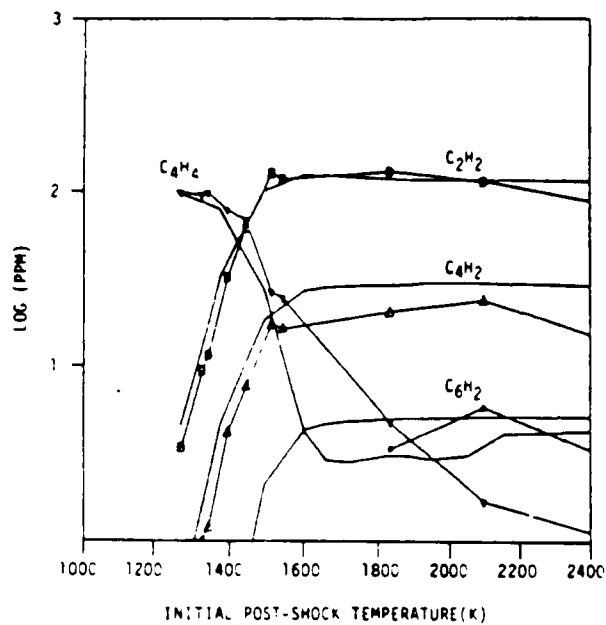


FIGURE 2 0.115% VINYLACETYLENE PYROLYSIS  
data vs. model, 700 microseconds

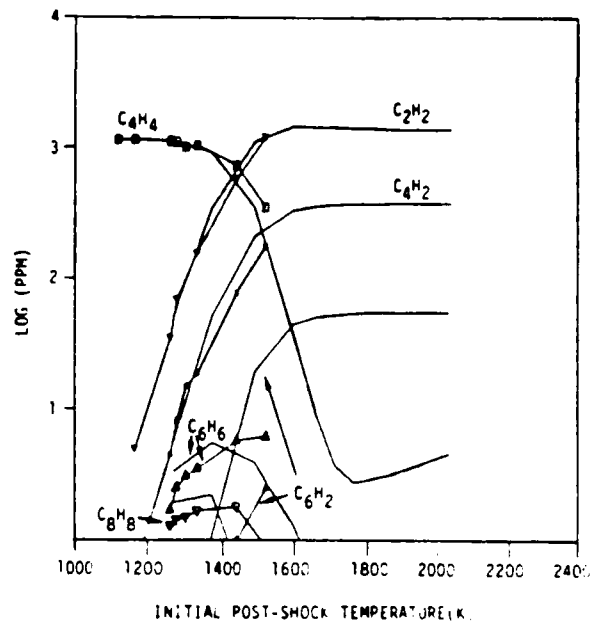


FIGURE 3 1% VINYLACETYLENE PYROLYSIS  
data vs. model, 700 microseconds, aliphatics

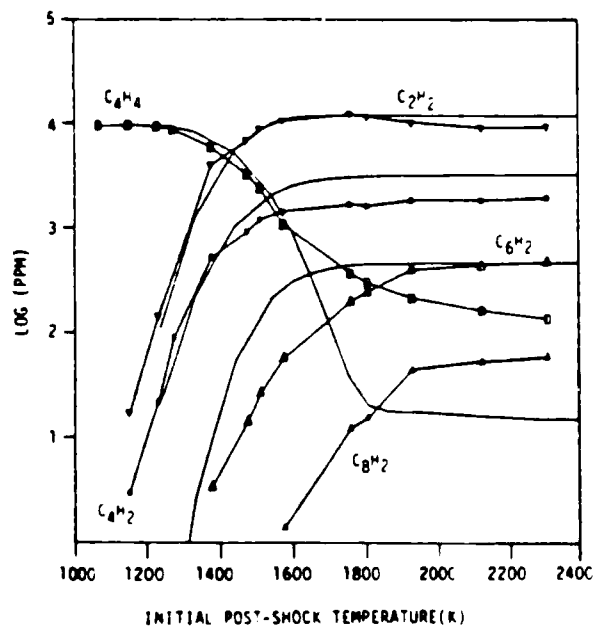
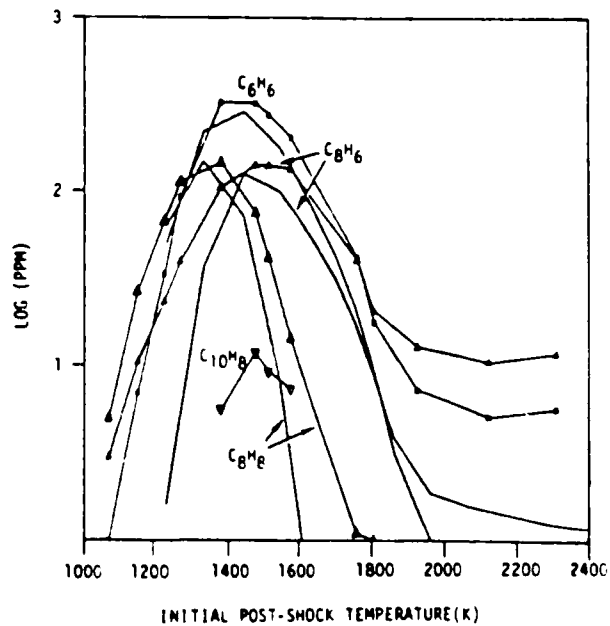


FIGURE 4 1% VINYLACETYLENE PYROLYSIS  
data vs. model, 700 microseconds, aromatics



## APPENDIX IV

### Pyrolysis of $C_6H_6$

by

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### Introduction

Several mechanisms for the pyrolysis of benzene at elevated temperatures have been previously proposed. Unfortunately, none of these mechanisms is entirely satisfactory when both experiments and thermodynamics are considered. Yet, knowledge of benzene decomposition will increase the understanding of the breakup and formation of other aromatic compounds. Consequently, a single-pulse shock tube (SPST) investigation of the pyrolysis of benzene has been performed over the temperature range of 1200 to 2400K. In addition, thermochemical estimates and detailed chemical kinetic modeling have been performed to evaluate the previously proposed mechanisms for benzene pyrolysis.

### Description of Facilities and Model

The 3.8 cm (i.d.) single-pulse shock tube (SPST) used in this experiment utilizes the "magic hole" technique for quenching pyrolyzed samples at rates above  $10^5$  K/sec. SPSTs were developed by Glick, Squire, and Hertzberg (1) and the UTRC facility has been described by Colket (2). Gas samples, after dwell times of approximately 700 microseconds, were automatically collected and analyzed for reactant and products using heated gas sampling valves and a Hewlett Packard 5880A gas chromatograph. With a CP Sil 5 CB (from Chrompack, Inc.) capillary column and a silica gel packed column,  $H_2$  and hydrocarbons up to  $C_{10}$  were identified and quantitatively analyzed.

Argon (99.999% pure) was obtained from Matheson and LC-grade benzene was obtained from the Burdick and Jackson Laboratory. The initial mixture concentration was 130 ppm benzene in argon and was prepared gravimetrically. Gas chromatographic analysis indicated that impurities included unidentified  $C_5$ ,  $C_6$  and  $C_7$  hydrocarbons as well as toluene, although the total concentration of impurity was less than 0.2% of the initial benzene.

Detailed chemical kinetics calculations are performed using CHEMKIN(3), LSODE (4), and a version of a shock tube code (5) which has been modified to include the quenching effects in a SPST. Quenching rates varied with shock strength and were calculated using measured pressure traces and assuming isentropic expansion. The modified code also allows monitoring of time-dependent contributions from each reaction to the formation and/or destruction of each species.

### Proposed Mechanisms

Mechanisms for the decomposition of benzene are listed in Table I. It is important to note that most are not single-step mechanisms. Radical intermediates equilibrate rapidly and their concentrations are sufficiently low to render them (nearly) undetectable in many systems. Experimental results from the present and previous high temperature works (6,7) suggest that primary stable products are acetylene, diacetylene, and hydrogen and the initial production rate of acetylene is two to three times higher than that of diacetylene. Unfortunately, this information is of minimal use in sorting out the mechanisms since benzene pyrolyzes at high temperatures (relative to pyrolysis temperatures of other hydrocarbons) and all intermediates shown in Table II rapidly pyrolyze to the approximate mixture of acetylene and diacetylene that has been observed.

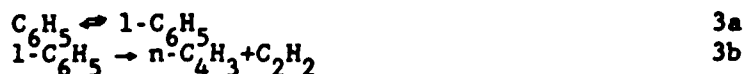
Mechanism A is the generally accepted reaction sequence; however, only Reaction 1 is understood. The breaking of the C-H bond is believed to be the initiation step in both pyrolytic and some oxidation studies. Its rate has been determined from D-atom production (in pyrolysis of  $C_6D_6$ ) (8) and from detailed modeling studies of both pyrolysis (9) and oxidation (10). An RRKM fit has been performed by Kiefer, et al (9) using available experimental data and is consistent with thermodynamics. Their  $k_1^\circ$  is given by  $10^{17.3} \exp(-118 \text{ kcal/RT}) \text{ sec}^{-1}$ . Knowledge of the mechanism for phenyl decomposition is substantially less than that for Reaction 1. Some information is available on the overall rate,  $k_3$ ; yet the details of the ring fracturing process have not been defined. The thermochemical estimate by Fujii and Asaba (11) has been until recently the most often quoted rate for this process. More recent modeling (8,9) of benzene pyrolysis has produced similar rates as Ref. 11; however, since Reaction 1 is rate limiting over most of the temperatures regimes examined, the modeling results for  $k_3$  are expected to be lower limit estimates with large uncertainties in the temperature dependence. The Fujii and Asaba (11) estimate,  $k_3 = 3.16 \times 10^{14} \exp(-86 \text{ kcal/RT}) \text{ sec}^{-1}$ , was based on an "old" value for the heat of formation for i- $C_4H_3$  of 102 kcal/mole (12); however, more recent estimates using group additivity (13) and BAC-MP4 (14) techniques fix this value closer to 115 kcal/mole. In addition, n- $C_4H_3$ , which has a  $\Delta H_f$  of 126 kcal/mole, is the preferred isomer for phenyl decomposition. Consequently, Reaction 3 is over 100 kcal/mole endothermic. If this process involves direct  $C_2H_2$  elimination, then the previous modeling efforts that produced lower limit rates strongly suggest that the high pressure A-factor is at least  $10^{17.8}$ . This value is orders of magnitude higher than what would be expected for this multibond process. Consequently, it must be assumed that Reaction 3 represents an overall process or that processes involving radicals other than, or in addition to, phenyl are important to benzene decomposition.

One alternative route for benzene decomposition is direct  $C_2H_2$  elimination (Mechanism B) and has received recent support (6,8); however, Kiefer, et al (9) have shown it is not necessary to invoke this step to describe experimental profiles. In addition, it should be noted that the direct elimination is a multibond process which should be unlikely, and presumably involves the intermediate formation of the  $C_6H_4$  diradical. For this intermediate, the effective activation barrier to Reaction 4 may be as high as 180 kcal/mole.

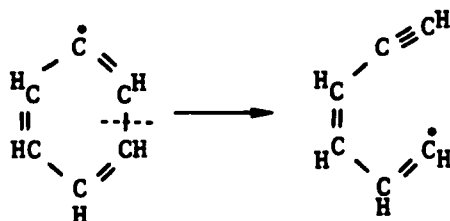
Another possible pyrolysis route involves the production of benzyne, which subsequently decomposes. Unimolecular decomposition of phenyl (Reaction 5) to benzyne is endothermic by 93 kcal/mole, which is nearly as much as Reaction 3. Similar thermochemical arguments can eliminate this decomposition route. The other route, Reaction 6, is a radical termination step and would produce an overall slowing of benzene pyrolysis. Knudsen cell pyrolysis experiments (7) have shown the formation of a  $C_6H_4$  compound. Assuming this compound is benzyne or another product of phenyl decomposition, Smith and Johnson (7) argued that  $C_6H_4$  is an important intermediate during benzene decomposition, especially at elevated temperatures. At least some of the product, however, may be composed of the chained isomers of  $C_6H_4$ . These isomers may be produced via hydrogenation of triacetylene, which was also observed in significant concentrations. Consequently, no clear evidence of the importance of Mechanism C is apparent.

Mechanism D appears to be very attractive, since an extrapolation of the rate coefficient (15) for H-atom addition to benzene (Reaction 8) is approximately an order of magnitude higher (Ref. 9) than H-atom abstraction (Reaction 2) at 1600 K. The addition reaction, however, competes with its reverse reaction. Using thermodynamics for  $c-C_6H_7$  derived from measurement of the forward and reverse rates of Reaction 8 (15), Mechanism D can be shown to have a negligible impact on benzene pyrolysis. However, a different set of thermodynamics for  $c-C_6H_7$  reported in Ref. 15 suggests that Mechanism D may play an important role at low temperatures. Detailed modeling calculations using Mechanism D were limited, due to what appears to be rather large uncertainties in both the heat of formation and entropy. Nevertheless, there are attractive features of this decomposition mechanism, especially at low temperatures, and it should be explored further. It is worth noting that Reaction 8 is not sufficiently energetic (only 16 to 26 kcal), that it can be followed immediately by Reaction 9 (71-81 kcal required). Instead,  $c-C_6H_7$  will collisionally thermalize prior to its decomposition to products. Only a minimal acceleration in rate due to the formation of an excited complex can be expected. Further exploration of this route (Mechanism C) should be performed.

With no fully satisfactory alternatives, and the expectation that phenyl must decompose to aliphatics at sufficiently elevated temperatures (when production of phenyl via Reaction 1 is fast), it is prudent to re-examine Mechanism A. One can separate Reaction 3 into the following sequence:



This sequence is the reverse of the processes suggested for the formation of phenyl during acetylene pyrolysis (17) and has been shown to compare favorably with recent experimental data (2). If one assumes that the ring breaks at the single bond as shown



then this is a relatively straightforward process analogous to the decomposition of  $n\text{-C}_4\text{H}_5$ ; i.e.  $\text{CH}:\text{CH}:\text{CH}:\text{CH}_2 + \text{C}_2\text{H}_2 + \text{C}_2\text{H}_3$ . Breakage of either of the other two single-bonds would require a more complex process involving H-atom shifting or the formation of energetic intermediates. The resultant linear compound would be expected to decompose to acetylene and  $n\text{-C}_4\text{H}_3$  or re-cyclize to phenyl. Detailed chemical modeling was performed using the reaction sequence in Table II coupled with an acetylenic mechanism similar to that reported (17, 18). A comparison of the model and single-pulse shock tube data is presented in Figure 1 for a series of shocks at an initial concentration of 130 ppm benzene in argon. In this figure, final concentrations produced after a dwell time of 700 microseconds followed by quenching are plotted as a function of initial post-shock temperature. Total pressure for these experiments is approximately seven atmospheres.

The comparison is quite reasonable. The higher fractional decomposition at low temperatures observed in the experiment may be due to impurities from the wall initiating the reaction at low temperature. The residual benzene observed experimentally at elevated temperatures may be caused by sampling a portion of the boundary-layer near the walls of the shock tube. The mechanism proposed in Table II is essentially consistent with Kiefer et al's except that Reaction 3 has been separated to 3a and b. An effective rate constant for Reaction 3 can be estimated by assuming a steady-state concentration for  $1\text{-C}_6\text{H}_5$ , i.e.

$$[1\text{-C}_6\text{H}_5]_{\text{s.s.}} = \frac{k_{3a}[\text{C}_6\text{H}_5]}{(k_{-3a} + k_{3b})}$$

$$\text{therefore } k_3^{\text{effective}} = \frac{k_{3a} k_{3b}}{k_{-3a} + k_{3b}}$$

This curved evaluation is depicted as a solid line in Fig. 2 over the temperature regime where sensitivity to this rate was observed. The curve is extrapolated to both low and high temperatures to facilitate comparisons to other evaluations. The relatively high values obtained in this work for  $k_1$  and  $k_3^{\text{effective}}$  are not surprising since the rate constant determined in these experiments are expected to be close to the high pressure limiting value.

### Conclusions

Previously proposed mechanisms for the pyrolysis of benzene at high temperatures have been reviewed using detailed chemical modeling and a brief thermochemical examination. The most widely accepted sequence,  $\text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5(+\text{H}) \rightarrow \text{C}_4\text{H}_3 + \text{C}_2\text{H}_2$ , is slightly modified to  $\text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5(+\text{H}) \rightarrow 1\text{-C}_6\text{H}_5 \rightarrow n\text{-C}_4\text{H}_3 + \text{C}_2\text{H}_2$  and the structure of the linear  $\text{C}_6\text{H}_5$  intermediate is proposed. Forward and reverse rates are consistent with thermochemistry and experimental data. A benzene decomposition route involving  $c\text{-C}_6\text{H}_7$  and  $1\text{-C}_6\text{H}_7$  was examined, yet sufficiently accurate thermochemistry was not available to reach final conclusions.



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TABLE I  
Previous Mechanisms for  
Benzene Pyrolysis

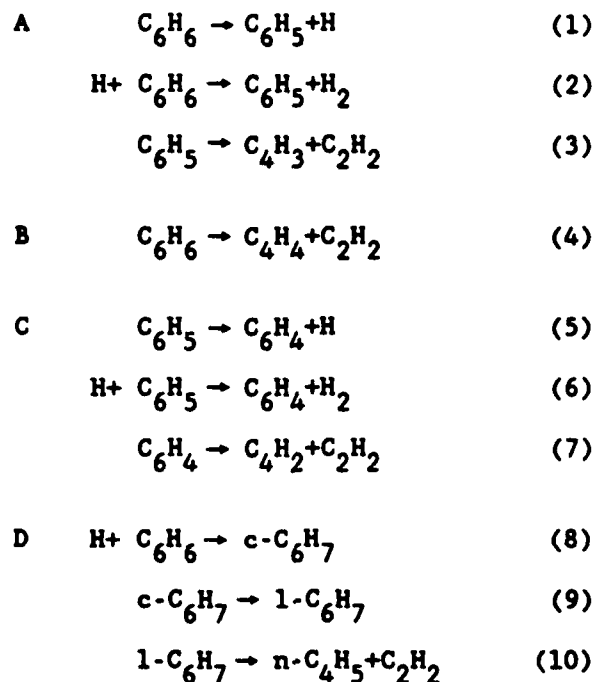


TABLE II  
Proposed Reaction Sequence  
for Benzene Pyrolysis

	<u>Forward rate</u>		<u>Reverse Rate</u>		
	$\log_{10} A$	$E$ cal/mole	$\log_{10} A$	$n$	$E$ cal/mole
1. $C_6H_6 \rightleftharpoons C_6H_5 + H$	16.18	107,900.	10.05	0.98	-5690.
2. $H + C_6H_6 \rightleftharpoons C_6H_5 + H_2$	14.40	16,000.	8.35	1.12	6420.
3a. $C_6H_5 \rightleftharpoons 1-C_6H_5$	14.00	65,000.	13.11	-0.68	3300.
3b. $1-C_6H_5 \rightleftharpoons n-C_4H_3 + C_2H_2$	15.34	38,000.	5.97	1.97	-3610.
11. $n-C_4H_3 \rightleftharpoons H + C_4H_2$	12.43	37,000.	11.29	0.44	-2790.
12. $n-C_4H_3 \rightleftharpoons C_2H + C_2H_2$	14.60	54,000.	7.89	1.66	-3120.
13. $C_2H + C_6H_6 \rightleftharpoons C_2H_2 + C_6H_5$	13.30	0	12.00	0	12520.

FIGURE 1. 130PPM BENZENE PYROLYSIS  
COMPARISON OF MODEL AND EXPERIMENT

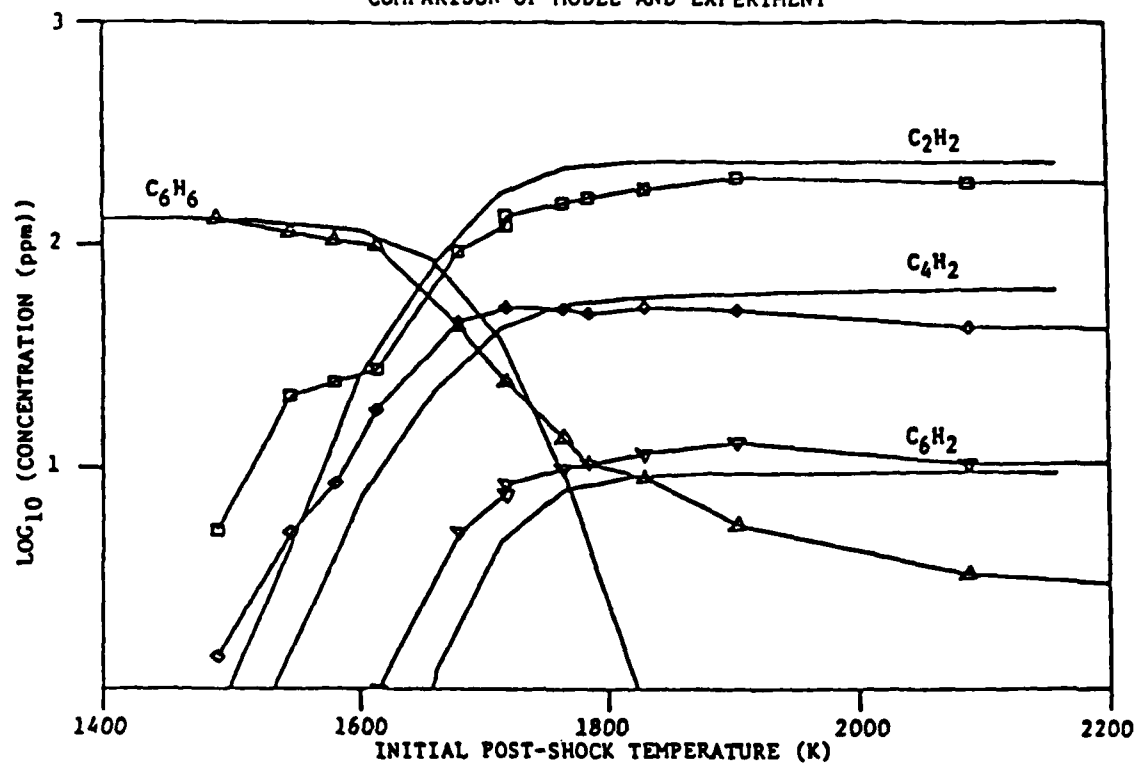
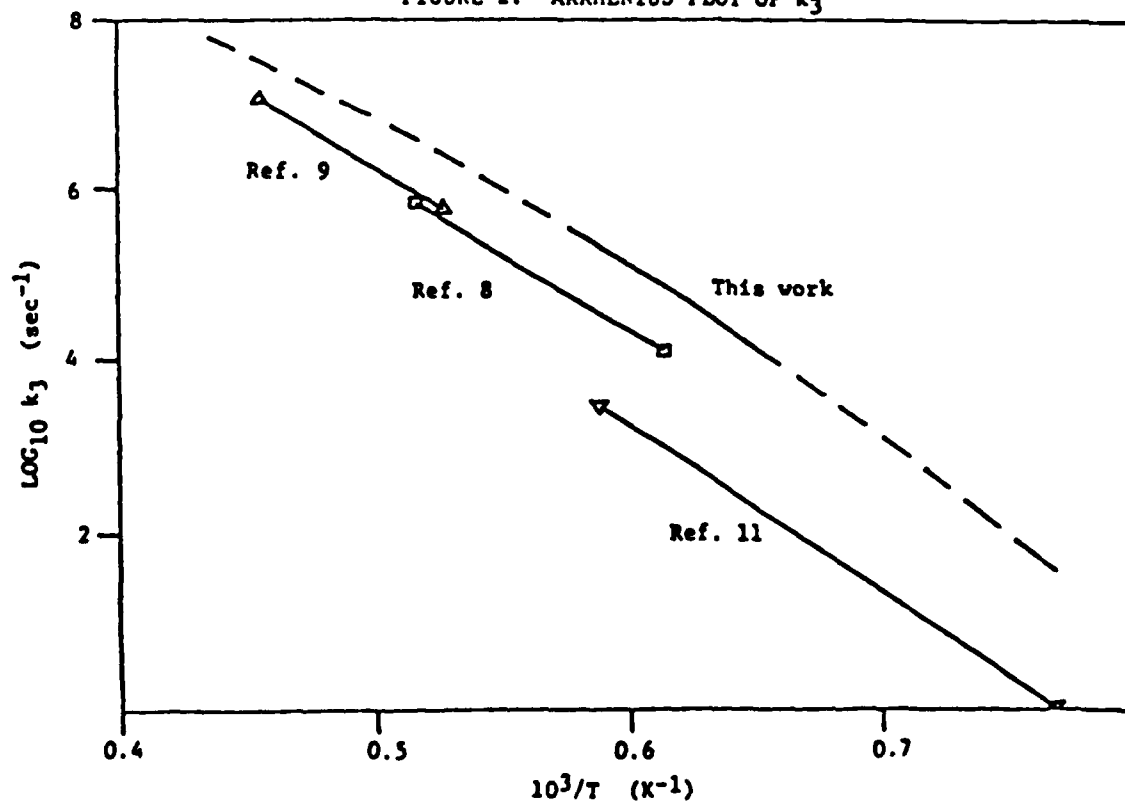


FIGURE 2. ARRHENIUS PLOT OF  $k_3$



END

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